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(54) **Thermoplastic polymer composition, products formed therefrom and an extruder for processing the composition.**

(57) A fire resistant non-halogenated and flexible polymer composition comprises a polymer mixture with an inorganic filler. The polymer mixture comprises

- as an elastomer component, an ethylene-copolymer or mixed polymerisate with a comonomer portion of at least 38% consisting of unsaturated ester comonomers, the elastomer being present in an amount by weight of least 50% of the polymer mixture,
- as a plastomer component an ethylene-copolymer with an ethylene portion of at least 70%, the plastomer component being present in an amount by weight of at most 50% of the polymer mixture. The filler is a metal hydroxide used in an amount of 180 to 320% of the polymer mixture.

The composition is particularly useful as sheathing for a cable.

An extruder for processing the composition is also described.

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THERMOPLASTIC POLYMER COMPOSITION PRODUCTS FORMED THEREFROM, AND AN EXTRUDER FOR PROCESSING THE COMPOSITION

The invention relates to a fire resistant, non-halogenated flexible thermoplastic polymer composition and to an extruder for processing such a composition.

For many applications, in particular, for cable sheathing, synthetic materials are required which are non-combustible or not easily inflammable and which have good mechanical strength. Since synthetic materials containing halogens cause secondary damage when burning due to the development of harmful gases, for example corrosive hydrochloric acid gas, combustible cross-linked polyethylene mixed with inorganic additives giving fire-resistance has been used. However, the manufacturing costs are relatively high in comparison with PVC for example, since adequate mechanical strength could only be achieved

by cross-linking. In addition, polyethylene is only receptive to fillers in a known degree, since with an excessively high filler content the mixtures become stiff, have inadequate mechanical cohesion and are difficult to process. The filling mixture known from German Offenlegungsschrift 25 54 802, which does not have to satisfy high requirements as regards mechanical strength, would not be suitable for example for cable sheathing or cable insulations.

It is an object of the invention to provide an economical polymer composition, which on the one hand is fire-resistant despite the absence of halogens and on the other hand has mechanical strength and can be processed satisfactorily.

According to the present invention there is provided a polymer composition comprising a thermoplastic polymer mixture based on ethylene polymers or copolymers, which is filled with inorganic fillers leading to fire-resistance and optionally containing further fillers and/or additives characterised in that the polymer mixture comprises - as an elastomer component an ethylene-copolymer or mixed polymerizate with a comonomer portion of at least 38% by weight consisting of unsaturated ester comonomers, the elastomer being present in an amount by weight of at least 50% of the polymer mixture, - as a plastomer component an ehtylene-copolymer with an ethylene portion of at least 70% by weight of the plastomer component being present in an amount by weight of at most 50% of the polymer mixture, and in that the filler is a metal

hydroxide in an amount by weight of 180 to 320% of the polymer mixture.

The term mixed/polymerisate as used herein covers polymers prepared from more than two comonomers.

Preferably the comonomer portion of the elastomer component is a vinyl acetate. This vinyl acetate is economical and produces a composition which can be processed particularly well.

Preferably also the elastomer component amounts to 60-80% of the weight of the polymer mixture. Such amounts of elastomer produce a high-strength composition which can be extruded without plasticiser.

The composition of the invention is particularly useful as sheathing or insulation for cable, (for example an electrical or communication cable). The material is preferably unfoamed in order to achieve the desired high mechanical properties.

The invention further provides an extruder for processing the polymer composition characterised by the use of a screw with the following features:

- a feed zone having a progressive core with a length of 7-17D, preferably 10-15D (D equals diameter of the screw), with a channel depth of 0.08-0.19D for $D > 90$ mm or 0.01D to 0.24D for $D < 90$ mm with a compression of 1:1.05 to 1:1.7, preferably 1:1.2 to 1:1.5,

- a low-compression metering zone with a length of 4-13D, preferably 5-8D, with a channel depth of 0.08-0.18 for D < 90 mm or 0.1D-0.22D for D> 90 mm with a compression of 1:1 to 1:1.2, preferably 1:1.

This extruder is particularly advantageous for processing the compositions according to the invention.

The thermoplastic or thermoelastic polymer composition according to the invention can be produced economically, since no cross-linking is necessary and the proportion of economical fillers is high. Nevertheless surprisingly high tensile strengths and compression strengths occur, which can even be higher than with PVC. The high degree of filling with metal hydroxides, such as aluminium hydroxide in particular, provides extraordinarily good fire-resistance (oxygen index). When used for cables, in the case of fire, an ash structure remains, which guarantees that the electrical insulating property is maintained. At a temperature of 850°C, emergency operating characteristics last for a period of at least twenty minutes, as was previously possible solely when using cross-linked synthetic materials.

The plastomer constituent of the composition according to the invention increases the mechanical strength on account of the high proportion of ethylene comonomer. Preferably the plastomer is present in an amount of at least 5% by weight of the polymer mixture. The high degree of filling

with metal hydroxide is possible with the addition according to the invention of the plastomer component, preferably ethylene vinyl acetate (EVA), or more preferably ethylene ethyl acrylate (EEA) or ethylene butyl acrylate (EBA) or a mixture thereof, in which case astonishingly high strength factors are achieved without cross-linking and despite an extremely high degree of filling with metal hydroxide.

The processing of the composition in mixers and extruders is very good despite the high degree of filling and without the use of plasticisers which are themselves normally flammable.

On account of the plastomer component, the temperatures during processing of compositions according to the invention, for example in a plunger kneading machine, must be greater than 100°C, but if possible greater than 120°C. However, since polar mixtures of this type tend to stick to metals the wall of the kneading machine must be cool during processing. In this case temperatures of less than 50°C are desirable and a temperature of 80°C should not be exceeded. If a parting compound is used, it should preferably be one of a fire-resistant grade.

When processing compositions according to the invention in an extruder, for example for the manufacture of cable sheathing, a particularly high throughput of material can be achieved without

problems if the extruder screw is constructed according to the invention. In this case it has been found that only two functional zones are necessary, namely a feed zone and a metering zone. Experiments with screws of different dimensions produced the result that, with the parameters indicated for the extruder screw according to the invention in which a low compression or even compression-free metering zone is important, high manufacturing speeds are possible with a relatively low drive power.

The advantageous properties of some compositions according to the invention are illustrated in the following non-limiting examples: The compositions of Examples 1 and 2 are particularly suitable for cable sheathing, that of Example 3 for strong inner cable sheathing and that of Example 4 for the core insulation of a cable. In the Examples EVA stands for ethylene vinyl acetate and VA for vinyl acetate.

Example 1

EVA-elastomer (40% VA)	65 parts
EVA-plastomer (9% VA)	35 parts
Aluminium hydroxide	200 parts
Anox HB, age resistor	1 part
Carbon black F.E.F.	2.5 parts

Tensile strength : 8 N/mm^2

Breaking elongation : 150%

Oxygen index greater than 45.

Example 2

EVA-elastomer (45% VA)	60 parts
Ethylene copolymer (0-20% VA)	40 parts
Parting compound	5 parts
Aluminium hydroxide	150 parts
Magnesium compound (magnesium carbonate and/or magnesium hydroxide)	50 parts
Flectol H age resister	1 part
TiO_2	1 part

Tensile strength : 7.5-9N/mm^2

Breaking elongation : 140-190%

Oxygen index approximately : 45-50

Example 3

EVA-elastomer (40% VA)	100 parts
Aluminium hydroxide	250 parts
Parting compound	5 parts
Age resister. AgeRite Resin D	1 part

Tensile strength : approx 5.N/mm^2

Breaking elongation : approx 200%

Oxygen index : approx 50

Example 4

EVA-elastomer (40% VA)	60 parts
Ethylene-copolymer (0-20% VA)	40 parts
Aluminium hydroxide (low in electrolyte) ..	200 parts
Age resister Vulkanox HS	1 part
PCD (Polycarbodiimide)	2 parts
Pigment	1 part

Tensile strength : 7-8 N/mm^2

Breaking elongation : 150-180%

Oxygen index : LOI $\geq$ 45

Example 5

EVA-elastomer (45% VA)	60 parts
EBA-copolymer (17% BA)	40 parts
Aluminium Hydroxide	150 parts
Magnesium Hydroxide	50 parts
Parting Compound	5 parts
ANOX HB, (Age Resister)	1 part
TiO_2	1 part

Tensile Strength : 8-9 N/mm^2

Breaking Elongation : 200% approx

Oxygen Index : >45

Example 6

EVA-elastomer (45% VA)	60 parts
EEA-copolymer (19% EA)	40 parts
Aluminium Hydroxide	260 parts
Flectol H Age Resister	1 part
Carbon Black FEF	2 parts
Parting Compound	5 parts

Tensile strength : 8-9 N/mm^2

Breaking elongation : 180-200%

Oxygen Index : 50 approx

In these mixtures, aluminium hydroxide with a specific surface of the particles of more than 6 m^2/gram was chosen. Particularly advantageous results for the oxygen index and strength occurred with specific surfaces of more than 10m^2/gram. Good results were also obtained when using magnesium hydroxide with a particle size of preponderantly $< 44\mu m$.

Naturally, additional fillers such as for example kaolin, talcum, metal carbonates such as chalk and magnesium carbonate can also be added to the mixtures according to the invention. Also other additives such as additional polymers, age resisters and auxiliary processing means can be added. The polymer mixtures according to the invention also have outstanding mechanical strength factors, even without cross-linking and withstand the strictest fire tests.

Cross-linking increasing the strength still further by means of a peroxide or by irradiation with high energy rays, is conceivable in special cases. Mixtures according to the invention have good electrical properties (for use as insulating mixtures) and therefore can also be used for high quality electrical cables such as communications cables, coaxial cables or high voltage cables. The compositions according to the invention are very suitable for jacketing or sheathing of cables with high quality thermoplastic insulations, such as energy cables, high frequency cables and telecommunication cables etc., and also those with insulations with air spaces (like PE-CELL and PE-DISC). In this case there is no danger of the core insulations deforming or melting, because the long residence time necessary in the case of CV-vulcanization, at high pressure and high temperature, is dispensed with. Naturally, the use of compositions according to the invention is not restricted to electrical cables, but can be used where ever economical, fire-resistant materials, which are mechanically strong without cross-linking, are required. Processing to form elongated, flat products such as sheets, tapes, foils and sectional members is quite possible. One such example of a flat product is one for use as a floor covering, e.g. a tile.

CLAIMS

1. A polymer composition comprising a thermoplastic polymer mixture based on ethylene polymers or copolymers, which is filled with inorganic fillers leading to fire-resistance and optionally containing further fillers and/or additives, characterised in that the polymer mixture comprises - as an elastomer component, an ethylene-copolymer or mixed polymerizate with a comonomer portion of at least 38% by weight consisting of unsaturated ester comonomers, the elastomer being present in an amount by weight of at least 50% of the polymer mixture, - as a plastomer component an ethylene-copolymer with an ethylene portion of at least 70% by weight, the plastomer component being present in an amount by weight of at most 50% of the polymer mixture, and in that the filler is a metal hydroxide in an amount by weight of 180 to 320% of the polymer mixture.

2. Polymer composition according to claim 1 characterised in that the comonomer portion of the elastomer component is a vinyl acetate.

3. Polymer composition as claimed in any one of claims 1 to 3 wherein the comonomer portion of the plastomer component is vinyl acetate, ethyl acrylate or butyl acrylate.

4. Polymer composition according to any one of claims 1 to 3, characterised in that in order to achieve a high-strength mixture which can also be

extruded without plasticizer, the elastomer component amounts to 60-80% of the weight of the polymer mixture.

5. A cable having sheathing or insulation produced from the composition of any one of claims 1 to 4.

6. An elongate product or a flat product formed from the composition as claimed in any one of claims 1 to 4.

7. A product as claimed in claim 6 which is a sectional member.

8. A product as claimed in claim 6 which is a floor covering, e.g. a tile.

9. Extruder for processing a mixture according to one of claims 1 to 4 characterised by the use of a screw with the following features:- a feed zone having a progressive core with a length of 7-17D, preferably 10-15D (D equals diameter of the screw), with a channel depth of 0.08-0.19D for $D < 90$ mm or 0.01D to 0.24D for $D > 90$ mm with a compression of 1:1.05 to 1:1.7 preferably. 1:1.2 to 1:1.5,
- a low-compression metering zone with a length of 4-13D, preferably 5-8D, with a channel depth of 0.08-0.18 for $D < 90$ mm or 0.1D-0.22D for $D > 90$ mm, with a compression of 1:1 to 1:1.2, preferably 1:1.

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